PATENT SPECIFICATION

818,412

Date of Application and filing Complete Specification: July 5, 1955. No. 19456/55.

Application made in United States of America on July 23, 1954.

Application made in United States of America on Nov. 1, 1954.

Complete Specification Published: Aug. 19, 1959.

Index at Acceptance:—Classes 2(6), P4D(2:3A:3B1), P4P1(B:C:E1:E5:F:X), P4P(2X:3:4C:6X), P7D2A(1:2A), P7P1(B:C:E1:E5:F:X), P7P(2X:3:4C:6X), P8D(1A:1B:2A:2B2:3A:5), P8P1(B:C:E1:E5:F:X), P8P(2X:3:4C:6X), P8T2(C:D); **96** B(14F:14X:19); **and 140,** A(2H:2N1:2N2:2N3:5G9:10B1:10B2:10B3:11F:16B3), E1(A:D:H), F2(B:C), P3(B:C:E:F4:G1:G4:G5).

International Classification:—B27k. C08f.j. D06m. D21h.

COMPLETE SPECIFICATION

Polymerization Process

We, TEE-PAK, INC., a Corporation organized and existing under the Laws of the State of Illinois, of 3520 South Morgan Street, Chicago 9, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved polymerization process and to the products produced thereby.

The treatment of polymeric materials, particularly in the form of films, fibres and filaments, in order to modify their physical and/or chemical characteristics has been given more and more consideration in recent times in attempting, by various treatments, to meet the ever-increasing demands for articles of this type, having certain desired fluid or vapour permeability characteristics, dyeing and printing qualities, and a variety of other properties such as strength, elasticity, flexibility, hardness and adhesion to other surfaces, to mention a few.

Some efforts have been made in the past to effect such changes in characteristics in polymeric films, fibres, or filaments by forming, *in situ*, polymers on the surfaces and within the gel phase thereof. Success has not been great due, at least in part, to an inability to control satisfactorily the nature and extent of the polymer deposition on or in the film being treated. In the interest of brevity and convenience, the term "film" as hereinafter used is intended to include fibres, filament and like articles and, in fact, any articles made of polymeric materials, whether natural or synthetic.

Generally speaking, the present invention has as one of its features a technique, a step or series of steps by which we are able to control the deposition of a polymer to a predetermined portion of either the solid or gel phase of the film being treated. Included in the process of our invention is the step or series of steps which involves the formation of a salt compound with the ion-exchange groupings in the material of which the film is formed in that portion, and only in that portion of the solid or the gel phase of that material where its presence is desired. The salt compound is selected so that it is from the group which normally acts as catalysts for polymerization and, accordingly, exposure of the thus-treated film to solutions or suspensions of monomer results in the deposition of polymers in the near neighbourhood of the catalyst.

According to the present invention, a method of producing a composite polymeric product comprises polymerizing a monomer *in situ* on and/or in a polymeric material which has ion-exchange capacity, in the presence of a polymerization-initiating catalyst system at least partially bonded to the polymeric material by ion-exchange forces.

In one preferred embodiment of the method of the invention, the polymeric material is contacted with a polymerization-initiating catalyst to bond the catalyst to the polymeric material by means of ion-exchange forces and the thus-treated polymeric material is then contacted with the monomer so as to polymerize the monomer *in situ*.

In another preferred embodiment of the method of the invention, the polymeric material is contacted with at least one but less than all of the components of a multiple-component polymerization-initiating

catalyst system to bond such component or components to the polymeric material by means of ion-exchange forces and the thus-treated polymeric material is then contacted with the monomer and with the remaining component or components of the catalyst system so as to polymerize the monomer *in situ*.

The invention also consists in a composite polymeric product obtained by depositing a polymer in and/or on a polymeric material having ion-exchange capacity, the concentration of deposited polymer in the product being greatest in the vicinity of the ion-exchange groups of the polymeric material.

In a preferred embodiment, the product, of the invention is obtained by polymerizing a monomer in less than the total volume of a solid or gel containing ion-exchange groups.

In another preferred embodiment, the polymeric material is wood fibre, whereby a modified wood fibre product is produced.

According to another preferred embodiment of the invention, the method comprises polymerizing an unsaturated monomer *in* situ in wood fibres in the presence of a cationic free-radical-producing, polymerization-initiating catalyst at least partially bonded to acid groups in the wood fibres by ion-exchange forces.

The present invention is applicable to the treatment of polymeric materials which possess a naturally-occurring ion-exchange capacity, such materials including, for example, cellulose, wool, paper, alginic acids and silk; the process is likewise applicable to the treatment of polymeric materials which have been modified by the artificial introduction of ion-exchange capacity into or on to the surface thereof by chemical reactions which are well known in the art. Materials and reactions included in the latter are for instance: the oxidation of polyethylene, cellulose acetate, cellulose, rubber and synthetic rubber sulphonation of polystyrene, replacement of the halo groups of polyhalostyrenes with amino groups, and a number of like processes which will suggest themselves to those skilled in the art.

An important feature of the present process lies in the fact that the polymeric material can be conditioned by a treatment, hereinafter described, so that polymer depositions thereon or therein can be directed to a selected portion of the solid or gel phase of that article. This localized deposition of polymer can be effected in several ways. One way is to treat the article so that ion-exchange groups are introduced to only a selected portion of a given phase of that article, in this way binding a catalyst only to that portion. Another way is to restrict, generally ultimate bonding to only a portion of the material being treated, if the ion-exchange groups are present throughout. The first method can be effected by using reagents to modify the desired portions of the article to be treated by introducing ion-exchange groups where the reagent itself cannot enter. An example of such a procedure would be the oxidation of the surface of polyethylene with warm chromic acid. Another example would be the topochemical reaction between fibrous cellulose and sodium chloracetate.

An example of the second procedure would be, for example, contacting cellulose (which contains carboxyl groups) with a solution of almost neutral ferrous iron for a very short time so that only some of the carboxyl groups in the cellulose are converted to the iron salt. The thus-treated cellulose may then be contacted with a solution of monomer in dilute hydrogen peroxide at a suitable temperature, polymerization then ensuing and being restricted to the outer portions of the cellulose gel.

Another procedure is to treat the polymeric material so as to exchange all of the groups in the solid or gel phase and subsequently pass the thus-treated material through an oxidizing or reducing agent in a sufficientlv short time so that only a part of the catalyst is destroyed, and that near the surface. In this way, catalyst placement is restricted to the interior of the film, polymer deposition occurring, then, where the catalyst is.

The general objective is to localize deposition of a polymer to a predetermined portion of the solid or gel phase of a polymeric material which possesses ion-exchange activity by a technique which permits this to be done more efficiently, economically, and with less waste monomer than heretofore possible.

Treatment of the polymeric material to effect ion-exchange, may be done in either aqueous or non-aqueous media. In certain instances, it might be desirable to swell the material before introduction of the catalyst; such swelling might be done in any solvent polar enough to dissolve even small amounts of the ionic salt catalyst.

While it is generally desirable to wash out the catalyst which has not become chemically combined with the polymeric film, filament or fibre, this is not always necessary. For example, if the polymeric article is immersed in a rather dilute catalyst solution, it can frequently remove the ionic species from the solution leaving almost no catalyst within the gel which is not chemically combined with the ion-exchange groups.

By the term "chemically combined" is meant that the material is present essentially as a salt and is bound to the ion-exchange groups by a salt bond.

Monomers which can be used in accordance with the present invention for "in situ" polymerization, include by way of example,

styrene, vinyl acetate, *n*-butyl acrylate, acrylic acid, *n*-octyl acrylate and acrylonitrile and, in fact, any type of addition monomer. Among the polymeric "host" materials which can be treated so that catalyst is bound thereto by ion-exchange forces, are those before mentioned as well as such materials as regenerated cellulose, felt, paper, wool, surface-oxidized polyethylene and the material known under the Registered Trade Mark "Saran".

In accordance with the present invention, addition-type monomers may be polymerized within a gel or solid phase of a polymeric material which may be in film, filament, fibre or any other form, by using the ion-exchange qualities of that material to anchor a catalyst within the desired phase; in this way there results very little waste of monomer which waste normally occurs when polymerization takes place within the fluid phase, due to escape of catalyst.

Cations as well as anions may be anchored to the solid or gel phase of polymeric materials, in accordance with our process. For example, the initiator of polymerization may be a single component (in the solvent), or it may be a complex initiator system, one of whose essential radical-producing components is an anion or a cation.

The following examples are illustrative of the principles of our invention:

EXAMPLE 1

Fifteen pieces of regenerated cellulose film made by the viscose process, and containing 0.025 milliequivalents of cation exchange capacity per gram of dry cellulose, about five mils thick in the gel state, and weighing about one gram were subjected individually to the following process:

The film was immersed at 25°C. for one minute in a solution of 0.7% ferrous ammonium sulphate at pH 5.4. The film was then washed in de-ionized water until a test showed that iron was not present in the washings and then placed in 400 ml. of 0.003% hydrogen peroxide in water at 100°C., the water containing 10 ml. of pure methyl methacrylate. Polymerization was continued for five minutes under reflux and was terminated by pouring the product into cold water. No clouding in the aqueous solution was observed. After extraction in acetone overnight and drying at 105°C. for several hours, the films were found to have increased in weight by 48%. The films were a slight yellowish brown in colour and were quite flexible. Mullen burst tests on the films indicated no decrease in strength, as compared with control films, and the test values were slightly over 6 pounds per mil per square inch of film area. The tenacity was about 3 grams per square mil as measured by the Scott test. Elongation had been decreased about one third as compared with a control film.

EXAMPLE 2

About 1 gm of a thinner film (1 mil) was treated with the ferrous solution as above described and washed to immobilize the ferrous iron catalyst by ion-exchange. The film was then placed in a 0.003% hydrogen peroxide solution at 100°C., the solution having on its surface ten ml. of pure styrene. The solution was refluxed for one hour and polymerization stopped as in Example 1. After extraction with toluene overnight and drying, the average gain in weight of several films was 36%. The films were slightly yellow, more brittle than the ones in which polymethyl methacrylate had been deposited, and more rigid. The surface was more hydrophobic than normal cellulose films.

EXAMPLE 3

Small sheets of Manila paper were used in this experiment. They were of very closely equal weight, and contained 0.1 milliequivalent of exchange capacity per gram. The papers were immersed in 0.7% ferrous ammonium sulphate solution at pH 5.4 for one minute, washed and added to a solution of 0.003% hydrogen peroxide containing 20 ml. of pure methyl methacrylate per litre of solution. The polymerization was continued at reflux for five minutes. Polmerization was stopped as in Example 1. The paper was dried and found to have increased in weight by 90%. It was a cream colour somewhat rigid, its dry Mullen strength was only about half that of the original paper, and its wet Mullen strength was about one and a half times its dry Mullen strength.

EXAMPLE 4

Manila paper was treated as in Example 3, except that a monomer solution of butyl acrylate was used instead of methyl-methacrylate. Polymerization time was twenty minutes. The film increased in weight by 44%, and was quite flexible even after having been dried at 110°C. overnight. A few of the sheets exhibited some adhesiveness.

EXAMPLE 5

Cellulose film containing 0.019 milliequivalents of exchange capacity per gram was dipped into 0.7% ferrous ammonium sulphate at pH 5.5 for one minute. It was rinsed to remove catalyst not chemically combined, and placed in a solution containing 0.03% hydrogen peroxide and 5% acrylonitrile at 100°C. and refluxed for one hour. After removal of the film and drying, it was found to have increased in weight by 30%.

EXAMPLE 6

Amino groups were introduced into cellulose by steeping the film in aqueous 2-chloroethylamine hydrochloride, blotting and placing in 50% sodium hydroxide solution at 100°C. for five minutes, according to the procedure of Guthrie, J. D. Textile Research J. *17*, 625, (1947). The films were then washed

with de-ionized water until neutral, and were found to contain 0.15 milliequivalents of anion exchange capacity per gram.

Persulphuric acid was made by passing ammonium persulphate through an Amberlite IR 120 cation exchange resin in its acid form ("Amberlite" being a Registered Trade Mark). The cellulose containing the amino groups was then steeped in the persulphuric acid for two minutes, washed to remove the uncombined catalyst, and then placed in 300 ml. of water containing 20 ml. of acrylonitrile at 50°C. for thirty minutes. After drying, the films had increased in weight by 23%.

EXAMPLE 7

Amino cellulose, produced as in Example 6, was steeped in 1% persulphuric acid for two minutes and washed free of excess uncombined persulphate at room temperature. A solution of 400 ml. of water containing 20 ml. of pure methyl methacrylate and 0.3 gm. of sodium bisulphite was prepared and heated to 60°C. The persulphate-treated film was then added and the system heated under air at 60°C. for fifteen minutes. After drying, the resulting films showed an average increase in weight of 65%.

EXAMPLE 8

A four foot long tube of regenerated cellulose film about four mils thick and three inches in diameter was tied at both ends. The tube was immersed for three seconds in an 0.7% solution of ferrous ammonium sulphate at a pH of 4.5 and 25°C., and then washed in de-ionized water to remove iron not chemically combined with the cation-binding capacity of the film. The film was then immersed in two litres of 0.003% hydrogen peroxide containing 25 ml. of pure methyl methacrylate, the solution being at the boiling point and kept at the boiling point under reflux for fifteen minutes. Polymerization was stopped by dumping into cold water. The film was then washed in hot water for several hours to remove excess monomer. Pieces of the film were cut out and the side of the film exposed to the ferrous catalyst solution was marked for identification. Several of the films were dehydrated in acetone and in alcohol. The methyl methacrylate polymer within the film was then converted to the acid hydrazide derivative by refluxing the film for seventeen hours with ten times its weight of hydrazine hydrate. The film was then washed for several hours to remove the excess reagent. Several pieces of film were placed in a sensitive Tollens reagent contained in an actinic glass vessel, pieces of film removed at intervals, and microscopic slides made of cross sections of the film. The films varied in colour with time from a yellow to deep red-brown. The cross sections showed that silver had been deposited within the film to a depth of only one fourth of the thickness of the film and from the side of the film which had been exposed to the catalyst.

Furthermore, other samples of the same pure cellulose film exposed to the same catalyst solution for three seconds, washed in de-ionized water to remove excess iron, dropped into 1% sodium sulphide for twenty minutes, dehydrated, and cross sections made, showed the green colour of ferrous sulphide precipitation penetrating into the film about the same distance as the band of precipitated colloidal silver metal. The film contained 0.031 millieq./gm. exchange capacity.

EXAMPLE 9

A solution was prepared, containing 400 ml. of water, 10 ml. of pure vinyl acetate and enough hydrogen peroxide to give the solution a 0.006% content of hydrogen peroxide. The solution was brought to 100°C. About 1.8 gm. of thin cellulose film containing 0.024 milliequivalents exchange capacity per gram of cellulose was steeped in 0.7% ferrous ammonium sulphate at a pH of 4.2 and washed to remove the uncombined iron. It was then dropped into the above solution and refluxed for five minutes. The equal increments of film were removed, dried after washing overnight at a temperature of 110°C. and had increased in weight by 2.3%.

EXAMPLE 10

This test showed that if the exchange capacity of the solid or gel phase were relatively high and the catalyst solution relatively dilute absorption of the catalyst into the film was relatively complete and very little, if any, uncombined catalyst was present in the gel phase. Thus, the washing step of the above examples could then be omitted.

Two mil thick cellulose film containing 0.06 m.e. of exchange capacity was used. The carboxyl in the films was in the acid form, i.e. the film had been treated with acid to convert any carboxyl present as salt into the free acids. About one gram was placed in a solution of 0.025% ferrous ammonium sulphate at pH 4.4. Within a minute, the pH had dropped to 3.6 because of ion exchange. The film was removed, blotted and immediately dropped into a boiling solution of 400 ml. of 0.003% hydrogen peroxide containing 10 ml. of pure methyl methacrylate. The solution was allowed to reflux for fifteen minutes. After stoppage of polymerization the dry film weighed 90% more than originally. No turbidity arose in the aqueous phase, thus indicating that there was no escape of catalyst ions.

EXAMPLE 11

Cellulose films about 14 mils thick and containing 0.026 m.e./gm. exchange capacity were dipped into 0.05M cupric acetate at 25 degrees for five minutes. The excess uncombined copper was washed out and the

films then immersed in an 0.05M solution of sodium hydrosulphite for two minutes. The film became purple due to colloidal copper. The films were then washed in warm water to remove the excess reagent, and immersed in a solution containing 20 ml. of pure methyl methacrylate and 1 g. of ammonium persulphate in 400 ml. of water. The film was left there at 25°C. for fifteen minutes, during which time the purple colour of the film was gradually removed and the film became only slightly translucent. When the film had been washed and dried, it was found to have increased in weight by 12%.

EXAMPLE 12

The same type of film as in Example 11 above was immersed in 0.01 N silver nitrate for five minutes. It was washed free of uncombined silver and immersed in 0.1% hydrazine hydrate in water for five minutes. Metallic silver was precipitated. The film was then washed and dropped into the same monomer system as in Example 11 and left to stand for fifteen minutes. The film was decolorized in about seven minutes and the film after washing and drying overnight at 110°C. had gained in weight by 2.2%.

EXAMPLE 13

Five samples of hygrostated wool varying in weight from 0.5—0.8 grams were steeped in 0.8% of persulphuric acid for twenty minutes at room temperature. The wool was washed to remove uncombined persulphuric acid. The washed wool was then placed in 400 ml. of water saturated with methyl methacrylate and also containing 0.3 grams of ferrous ammonium sulphate hexahydrate. The wool was left in the solution at 25°C. for nineteen hours. The wool fabric pieces were then removed, washed in water and dried. They had gained in weight by 111%. The wool samples were brownish in colour and had a stiff and harsh feel. No polymerization had occurred in the aqueous phase although some turbidity due to hydrolyzed ferrous ion was evident. Microscopic examination showed that the scales of the wool had been largely covered with polymer.

EXAMPLE 14

U.S.P. agar agar was used to make up a 4% gel in hot water. The gel solution was kept just above its lique-faction range of temperature while small amounts were poured into Petri dishes and allowed to solidify for about 30 minutes at room temperature. The thin disc of gel was removed from the dish and immediately weighed. The discs were between 1 and 3 millimetres thick and of such size, that they contained from 0.3 to 0.7 grams of the dry agar agar. The discs were then broken up into four pieces and stirred for twenty minutes with 200 ml. of a freshly prepared 0.7% ferrous ammonium sulphate solution which was 0.1% in ferrous iron. The discs were then removed from the ferrous solution and washed four times, for ten minutes each time in cold de-ionized water.

The films were then dropped into 200 ml. of dilute hydrogen peroxide containing 10 ml. of pure methyl methacrylate monomer. Polymerization was allowed to continue for various times, the results of polymerization at 24°C. and in the presence of 0.012% hydrogen peroxide being shown in Table 1 below. The results of polymerization with the same concentration of monomer and 0.006% hydrogen peroxide are shown in Table 2 below.

TABLE I.

DEPOSITION OF POLYMETHYLMETHACRYLATE INTO AGAR AGAR GELS*

	Agar Agar Weight, grm.	*Polymerization Time, hr.*	*Agar Agar plus Polymer Weight, gm.*	*Gain in Weight, %*
	0.4512	3	1.4317	214
	0.5282	3	0.9690	83
	0.4785	3	0.8687	82
	0.3312	4	1.4890	350
	0.4085	2	1.0492	190
	0.3065	2	0.6714	121
	0.2608	1.5	0.5780	122
Blanks:				
	0.4306	2	0.4012	
	0.5909	17	0.5112	

*Solution at 24°C. containing 5 per cent monomer and 0.012 per cent hydrogen peroxide.

TABLE II.

DEPOSITION OF POLYMETHYLMETHACRYLATE INTO AGAR AGAR GELS*

	Agar Agar Weight, gm.	*Polymerization Time, hr.*	*Agar Agar plus Polymer Weight, gm.*	*Gain in Weight, %*
	0.5338	0.83	0.6980	31
	0.5602	1.50	0.9721	73
	0.5358	2.00	1.1753	119
	0.6830	2.67	1.6880	147
	0.6713	3.17	1.4099	110
	0.4961	50.00	4.7240	851
	0.4529	50.00	3.6280	701
	0.3875	50.00	2.6385	580
Blank:				
	0.5908	50.00	0.5172	

*Solution at 24°C. containing 5 per cent monomer and 0.006 per cent hydrogen peroxide.

The ion-exchange capacity of the particular agar agar sample used was determined by steeping several thin gels of known agar agar content in 2 N.hydrochloric acid, washing to a pH of 5.5 in de-ionized water and titrating the acid form of the gel in the presence of 10% sodium chloride solution. A dilute standard, 0.021 N.hydrochloride acid solution was used and an acid-binding capacity (exchange capacity) of 0.5 milliequivalents per gram was found.

When the agar agar gel was placed in a 0.1% ferrous solution for the same time as was used in the polymerization, the gel washed, and the iron then displaced with acid, it was found that the sulphate group would combine with iron to about 95% of its capacity at the pH level used.

Sulphur was determined in the same lot of agar agar by means of Parr Bomb oxidation and turbidimetric determination of the sulphate formed in this way. The polymer was found to contain 0.64% sulphur, thus accounting for about 0.4 milliequivalents per gram of the exchange.

In the above procedure, no polymerization occurred in the aqueous phase.

Polymer in the gel discs was determined by soaking the discs in methanol for one half hour, decanting and then drying overnight at 55°C. The discs were then placed in a vacuum desiccator over phosphorus pentoxide at about 30°C. overnight.

EXAMPLE 15

Five ml. of p-chlorostyrene, freed of inhibitor by high vacuum distillation, was added to 100 ml. of 0.006% hydrogen peroxide in boiling water in a glass ground neck flask. One gram of regenerated cellulose film which had been steeped for one minute in 0.7% ferrous ammonium sulphate at pH 5.4, and washed, was added to the flask and the contents refluxed for twenty minutes.

The cellulose film was slightly hydrophobic and had gained in weight by 10% after drying. The initial cellulose had about 0.020 milliequivalent for carboxyl per gram cellulose. The film was a slightly yellowish colour.

EXAMPLE 16

The procedure of Example 15 was repeated except that the cellulose film was dipped for only three seconds in the ferrous solution. The very slightly yellow films obtained had gained in weight by a little less than 0.5% but were quite hydrophobic. A drop of water placed upon them did not spread and had a high contact angle with the film. In the case of a closed cellulose tube subjected to the above procedure, the tube could be wetted from one side and not from the other.

EXAMPLE 17

The procedure of Example 15 was repeated except that xylene was used as the solvent and 0.05% benzoyl peroxide as catalyst in xylene. In this instance, the cellulose tube increased in weight by 0.7% and had a somewhat non-uniform deposition.

EXAMPLE 18

Example 15 was repeated except that 2-5 dichlorostyrene monomer was used. In this case, the film weight increased by 15% and the film became somewhat stiff, a darker yellow in colour and showed somewhat more hydrophobicity.

EXAMPLE 19

Example 16 was repeated except that 2,5-dichlorostyrene was used. The surface of the film became completely water repellent. The film became a light yellow and increased in weight by about 1.2%.

EXAMPLE 20

Example 17 was repeated except that 2,5-dichlorostyrene was used as the monomer. Polymer deposition amounted to about 1.4%.

EXAMPLE 21

Water was removed from a 1.9 mil thick regenerated cellulose film by boiling the film for ten minutes apiece with three 300 ml. portions of methanol. A methanol solution of ferrous iron was prepared (containing very little water) by dissolving enough ferrous sulphate heptahydrate to give the solution a concentration of 0.1% ferrous iron. The solution was a very light yellow colour. Cellulose film dehydrated as above was added to the methanolic ferrous solution for five minutes with occasional stirring.

After rinsing once for five minutes, the cellulose was dropped into 300 ml. of boiling

methanol, containing 3.03% hydrogen peroxide and also containing 5 ml. of styrene monomer dissolved in the solution. Polymerization was allowed to continue at the boil for thirty minutes. After removal and drying overnight, the cellulose films were found to have increased in weight by 2.5%.

EXAMPLE 22

It was found that anhydrous methanol would dissolve 77 p.p.m. of ferrous iron as ferrous ammonium sulphate (essentially anhydrous). Example 21 was repeated except that this anhydrous medium was used in the ion exchange. The films resulting therefrom showed an increase in weight of 1.8%. They were a very faint yellow colour and did not seem to differ appreciably in hygroscopicity from cellulose after they had been exposed to water to plasticize them.

EXAMPLE 23

Example 21 was repeated except that the cellulose film containing the ion-exchange groups was steeped in the methanolic ferrous solution for only ten seconds before being subjected to styrene deposition. The films obtained in this manner showed an extremely hydrophobic surface as judged by the contact angle of water drops on the surface.

EXAMPLE 24

N,N - dimethyl - amionethyl - acrylate was freed of inhibitor and the monomer acetate was made by dissolving 5 ml. of the monomer in acetone and precipitating the acetate salt with 5 ml. of glacial acetic acid. Excess of acid was removed by washing the salt with ether. The salt was then made up to about 50% in water.

One gm. of cellulose film containing 0.03 milliequivalents of carboxyl per gram cellulose was steeped in 0.7% ferrous ammonium sulphate at room temperature and pH 5.5 for one minute and washed with de-ionized water to remove the salt not chemically combined.

Ten ml. of the above aqueous solution of the monomer acetate was added to 100 ml. of boiling 0.03% hydrogen peroxide. The treated cellulose film was added and refluxing allowed to proceed for fifteen minutes. The slightly yellow solution of the monomer remained clear during the polymer deposition. After the film was removed and washed with hot water for several hours and dried overnight at 110°C., it was found to have increased in weight by 6.3%. The film remained flexible, and showed ability to be dyed with acid dyes.

EXAMPLE 25

When the procedure of Example 24 was repeated except that the monomer base itself was used, polymer deposition was 3.8% of polymerization seemed to have taken place in the aqueous phase.

EXAMPLE 26

The procedure of Example 24 was repeated except that the cellulose films were treated only three seconds with the ferrous catalyst solution before being subjected to polymer deposition. A polymerization time of one hour was used. The films obtained increased in weight by 1.4%. Cross sections of the film dyed with an acid dye showed that the polymer deposition was mainly limited to the surface layers of the cellulose film.

EXAMPLE 27

In an effort to modify the surface layers of cellulose film so that it could be heat sealed to other film and so that it could be printed with some printing inks which do not stock to cellulose, the effect of deposition of *n*-butyl acrylate, *n*-butyl methacrylate, and *n*-octyl acrylate as thin layers into the surface layers of cellulose and on to the surface was investigated.

Cellulose film containing 0.025 milliequivalents of carboxyl per gram cellulose was steeped for five seconds in a 0.1% ferrous iron solution and washed free of uncombined iron. The film was dropped into 400 ml. of 0.03% hydrogen peroxide which contained 10 ml. of the monomer in question. Polymer deposition was allowed to take place for thirty minutes. The films were removed, washed thirty minutes in hot water and dried as tubes which had been blown up. The polybutyl acrylate and methacrylate modified films were somewhat dry to the touch with a small amount of tackiness in some areas of the film. The films into which polyoctyl acrylate had been deposited were quite tacky.

About 5.7% polymer had been deposited into the film containing polybutylacrylate, and 3.4% into those containing the methacrylate. About 2% polyoctyl acrylate had been deposited.

The films showed an increasing degree of hydrophobicity as the length of the carbon chain of the monomer was increased.

Heat seals of the material known under the Registered Trade Mark "Pliofilm" (rubber hydrochloride) to the cellulose film modified by deposition of butyl acrylate and methacrylate into and on to its surface were excellent for a short time. That is, the strength of the seal was greater than the thin "Pliofilm" film for a period of about one hour, but decreased in strength with time. The initial strength of the heat seal between cellulose modified with polyoctyl acrylate on its surface and "Pliofilm" was excellent and it lost strength but little with time.

EXAMPLE 28

The method of Example 27 was repeated except that the cellulose was treated with the ferrous iron for one minute to impregnate it completely. The known weights of cellulose increased by 30%, 23%, and 11% for the butyl acrylate, methacrylate and octyl acrylate respectively. The oven dry film con-

taining the poly *n*-butylacrylate was more flexible than the dry cellulose control film.

EXAMPLE 29

Hydroquinone inhibitor was removed from allyl acrylate monomer by extraction with concentrated, cold sodium carbonate solution and the excess alkalinity removed with sodium bicarbonate solution. Cellulose film was steeped for one minute in 0.1% ferrous iron solution at pH 4.5 and washed. Two ml. of monomer was added to 50 ml. of boiling 0.06% hydrogen peroxide. The treated film was added and allowed to react for one hour at the reflux temperature. After removing the film and washing with hot water, the film was found to contain unsaturation as shown by bromination experiments. The film had gained in weight by 5.4%. After the film was left for several days exposed to air and ultraviolet light, the amount of unsaturation had decreased to 20% of former values. The film had also become less flexible than formerly.

EXAMPLE 30

The procedure of Example 29 was repeated except that the cellulose film was steeped for only five seconds in the catalyst solution. The film gained in weight by only 1%.

Allylacrylate monomer, obtained from Monomer-Polymer Corporation, Leominster, Massachusetts, was distilled under 80 millimetres mercury pressure at 70°C. to free the monomer from inhibitor. Twenty 3″ pieces of regenerated cellulose film were dried and weighed and then treated in accordance with the procedures set forth in the following examples.

EXAMPLE 31

Four 3″ pieces of regenerated cellulose film were steeped in a solution of 0.1% ferrous solution at a pH of 5.4 for two minutes. The pieces of film were then freed of uncombined iron by washing, and were then placed in 200 ml. of boiling water containing 2 ml. of allylacrylate; the solution was made to 0.03% hydrogen peroxide immediately. The deposition was allowed to progress for one hour. After refluxing the films in the solution for one hour, they were removed and washed for thirty minutes in hot water. Two of the films were dried for determination of the extent of polymer deposition while the other two were reserved for strength measurements. The films were found to have increased in weight by approximately 36%; there was no marked difference in the appearance of the films compared with the controls. The treated films appeared to have much less stretch before breaking than the normal films.

EXAMPLE 32

Ten films were subjected to the conditions of Example 31 except that only 0.003% hydrogen peroxide was used. The films gave no evidence of surface deposition of polymer. Three of the films dried at 110°C. for three hours showed 11.4% increase in weight.

EXAMPLE 33

The following example illustrates the deposition of polymer which is localized to the outer portions of the cellulose film.

In this procedure, a regenerated cellulose film was steeped in 0.1% ferrous solution at a pH of 5.4 for three seconds. The film was in the form of a tube about 4′ long which had been tied at both ends. The tube was rinsed and placed in 400 ml. of 1% by volume boiling allylacrylate. Sufficient hydrogen peroxide was added to make the solution 0.03%, and deposition was continued for one hour. The film was then washed in the usual way.

By way of illustration of the localization of the deposition of the polyallylacrylate to one side, the film was placed in 0.02 N potassium permanganate solution for thirty minutes at room temperature. The film began to discolour and turn brown resulting from the oxidation of the unsaturated bond by the permanganate, and the consequent precipitation of manganese dioxide. Sections of the coloured film were washed thoroughly in hot water and dehydrated in acetone. Pieces were cast in wax and cross-sections made for purposes of microscopic study. It was found that the orange-brown colour was present only slightly on the side of the film representing the inside of the tube.

EXAMPLE 34

Regenerated cellulose film was washed free of glycerol and the free sulphur therein was removed by extraction with sodium sulphide followed by washing. Ten portions of this film were then dipped in ferrous solution, as in the foregoing examples, for three seconds, washed, and allylacrylate was deposited from 1% monomer solution and 0.003% hydrogen peroxide solution under reflux, for thirty minutes.

After drying, the sections of film were found to have increased in weight by 18%.

Immersion of the films in 0.02 N. potassium permanganate for thirty minutes, washing, dehydrating and cross-sectioning in wax as in the foregoing example gave microscopic cross-sections which indicated clearly that the yellow colour due to precipitated manganese dioxide was restricted to the outer layers of the cellulose gel.

EXAMPLE 35

The following example serves to show the presence of unsaturation in the cellulose film which has been modified in accordance with the present invention.

Two equal portions of about 1.00 grams of regenerated cellulose film, which had been modified by treating it in accordance with the procedure of Example 31, and an unmodified control film were placed in 50 ml.

of water. Saturated bromine water was added to the films in the dark. The unmodified film absorbed about 5 drops of bromine water while the modified film continued to absorb 5 times that amount.

The tables below illustrated the physical characteristics of treated and untreated film as indicated by the Scott and Mullen tests.

TABLE 3.

MULLEN TESTS OF CELLULOSE FILMS MODIFIED WITH VARIOUS AMOUNTS OF POLYALLYLACRYLATE

Film		Mullen Test, lb./sq. in./mil High	Low	Average
1	36 per cent made in 0.03 per cent peroxide ..	8.14	7.08	7.46
2	13 per cent made in 0.03 per cent perioxde ..	8.19	7.50	7.73
3	11 per cent made in 0.003 per cent peroxide ..	8.38	7.65	8.05
4	11 per cent localized to outer portions of film 0.03 per cent peroxide	8.03	5.57	6.85
5	11 per cent localized to outer portions of film 0.003 per cent peroxide..	9.00	7.35	8.55
6	Control Film	8.43	7.71	8.03

TABLE 4.

SCOTT TESTS OF FILMS INTO WHICH HAVE BEEN DEPOSITED VARIOUS AMOUNTS OF POLYALLYLACRYLATE

Film		Elongation, % High	Low	Average	Tensile Strength High	Low	Average
LONGITUDINAL :							
1	36 per cent Polymer ..	30	20	25	3.7	2.6	3.2
2	13 per cent Polymer ..	40	20	31	3.12	2.08	2.60
3	11 per cent Polymer ..	42	28	37	3.75	2.10	2.92
4	Control	55	45	50	3.2	2.6	2.92
TRANSVERSE :							
	Control Film	115	60	90	2.75	1.26	2.20
	11 per cent Polymer ..	85	50	73	2.30	1.37	1.87

It is seen from the above that there appears to be no great difference in the burst and tensile strength of the modified or control film.

The effect of polymer deposition on elongation is clear; it can be seen for example that, with a 36% deposition of polyallylacrylate in the cellulose, the longitudinal elongation is about half of that of the normal control film. It is also to be noted that the deposition of polyallylacrylate into the cellulose is much more effective in reducing the elongation at the break point than is the introduction of polymethyl methacrylate.

Besides allyl acrylate, other unsaturated monomers which can be deposited into cellulose and used in a manner similar to allyl acrylate are as follows:

Allyl Methacrylate
N,N-Diallyllacrylamide
Diallyl Adipate
Diallylamine
Diallyl Benzenephosphonate
Diallyl Diglycolate
Diallyl Fumarate
Diallyl Homophthalate
Diallyl Itaconate
Diallyl Maleate
Diallyl Malonate
Diallyl Melamine
N,N-Diallylmethacrylamide
Diallyl Oxalate
Diallyl Phthalate
Diallyl iso-Phthalate
Diallyl tere-Phthalate
Diallyl Sebacate
Diallyl Succinate
Divinylbenzene
Divinyl Ether of Diethylene Glycol
Ethylene Diacrylate
Ethylene Dimethacrylate
Glyceryl Trimethacrylate
Methallyl Acrylate
Methallyl Methacrylate
N,N-Methylene-bis-acrylamide
Tetraethylene Glycol Dimethacrylate
Tetramethylene Diacrylate
Tetramethylene Dimethacrylate
Triallyl Aconitate
Triallyl Cyanurate
Vinyl Acrylate
Vinyl Methacrylate

Those of the above compounds which have two or more unsaturated groups of similar reactivity can frequently be copolymerized and leave one group still unsaturated. This would be possible for example with allyl methacrylate; additional unsaturated bifunctional or polyfunctional monomers which could be used are trimethallyl phosphate, diallyl benzene phosphonate, ethylidene dimethacrylate, methylene dimethacrylate,

tetraallylpentaerythritol, crotyl methacrylate, acetylene tetramethacrylate, resorcinol dimethacrylate, chlorallyl methacrylate and ethylene glycol dichloroacrylate, to mention a few.

Among the possible applications of the deposition of a polyfunctional monomer into cellulose or other plastic or gel phase may be mentioned the following:

Copolymers of acrylate or methacrylates with an acid or basic polymer such as acrylic acid or vinyl pyridine could be made. Ion-exchange of a catalytic cation on to the outer layers of an object formed from such a resin permits, for example, rapid deposition of a polyfunctional cross-linking monomer into the surface layers for hardening them.

Flame resistance can be secured by the deposition of diallylbenzene phosphonate or similar compounds into the surface layers of cellulose or other polymer phase or into the interior. Copolymerization of this monomer with another may be used in order to speed the reaction and to secure a cross-linking.

An unsaturated surface may be obtained by the deposition of an unsaturated polymer like polyallylacrylate into the surface layers of cellulose or other polymer. The resulting unsaturation may be used in order to secure, for example, adhesion of an ink to the cellulose or other polymer surface by an oxidative cross-linking reaction. Unsaturated polymers deposited into the surface of an object to be printed leave unsaturation available for cross-linking with the unsaturation present in the ink vehicle. Thus a chemical bond instead of a phyical one is present between the ink or other coating and the cellulose or other film on or in to which has been deposited the unsaturated polymer.

Any one of a number of several rubber compounds or rubber elastomers can be coated on to cellulose or other film containing an unsaturated polymer deposited into the other layers of the object in question. The elastomers in solvents can be used to secure good contact between the elastomer and the unsaturated polymer treated surface.

A specific example of the above general technique is securing " adhesion" of rubber to a surface-treated rayon tyre cord.

The unsaturated polymer may be used after deposition for obtaining cross-linking with the phase into which it has been uniformly deposited. In spite of the fact that the cross-linkages may be only between the molecules of the polymer deposited, it results in a more brittle composition than normal. An example of this is polyallyl methacrylate deposited into acetone-swollen cellulose acetate films and then exposed to air and ultraviolet light. Cross-linking of the unsaturated polymer within the given phase can be achieved by thermal or oxidative cross-linkage.

Furthermore unusual decorative effect can be achieved by means of deposition of unsaturated polymers. For example, a solvent-swollen gel containing ion-exchange groups can be printed with a designed roller dipped in catalyst cation or anion soluton, and the unsaturated polymer then deposited by conventional means. The unsaturated polymer may itself be coloured, or may be reacted subsequently with a reagent giving a colour with the unsaturation. This can be achieved, for example, by the above-described reaction using potassium permanganate in neutral solution; in this manner, one can even make a three dimensional effect in an essentially homogeneous gel phase.

After deposition of an unsaturated polymer in a pattern into a gel phase, the subsequent cross-linkage of the unsaturation gives rise to unusual surface effects, i.e., a matte appearance caused by the unequal swelling of the treated and untreated material.

Chemical treatment of the unsaturation thus obtained is not, of course, limited to thermal or oxidative cross-linking, and chemical additions to the double bond can be used further to modify the host-guest polymer composition. Reactions with dienes, addition reaction with active hydrogen compounds like amines, ammonia, alcohols, phenols, mercaptans, hydrazine and phenyl hydrazine acids and so on will occur to those skilled in the art.

Furthermore adhesion to other films to achieve laminates can be effected by cross-linking with the use of addition reagents or by oxidative polymerization reactions.

EXAMPLE 36

Five percent acrylamide solution was made up in water containing a cellulose film which had been steeped in a chromium potassium sulphate solution containing 0.1% chromous ion, and washed. The mixture was made up at 50°C. and then made 1% in potassium persulphate. Reaction was allowed to continue for two hours at 50°C. When the film was washed with water and dried overnight at 110°C., it was found to have increased in weight by 10%, and was flexible and hydrophillic.

EXAMPLE 37

The procedure of Example 36 was followed except that the cellulose was steeped in 0.1% manganous, instead of chromous, solution. The manganous solution was present as manganous sulphate. The films were found to have increased in weight by 12%.

EXAMPLE 38

The procedures of Examples 36 and 37 were repeated except that the cellulose film was contacted with the respective cation solution for only five seconds before washing and placing in the aqueous monomer solution. With the chromous ion, the cellulose increased in weight by 1.3% and with the

manganous ion by 1.8%. Observation of cross sections of the films under polarized light indicated localization of the polymer deposition to the surface layers of the film.

EXAMPLE 39

Cellulose film which had been soaked in 0.7% ferrous ammonium sulphate at 250°C. for one minute and washed, was dropped into a solution of 2% bismethyleneacrylamide in 50:50 v/v acetone-water which was 0.03% in hydrogen peroxide. The solution was at the boil when the film was added. Polymerization was allowed to continue for thirty minutes. About seven minutes after the start of the polymer deposition, the aqueous phase became cloudy and an appreciable amount of a white jelly had formed when the polymer deposition had ended.

The jelly was wiped off the cellulose film and the film extracted for several hours in hot acetone. After drying, the film was found to have increased in weight by 5.3%. It was less flexible at a given equilibrium moisture content than cellulose control films. The Mullen strength was about 10% above that of the control films.

EXAMPLE 40

The procedure of Example 39 was repeated except that the film was steeped for only six seconds in the ferrous iron. In this instance, the weight increased by only 1.4%. The films when wet after drying showed a puckered surface.

EXAMPLE 41

Beta-amino-ethyl-acrylate was made by direct esterfication af acrylic acid. The monomer was used to deposit into cellulose by a procedure similar to that employed for Example 25. It was found that the films had increased in weight by 18%. The films could be fast dyed with dyes such as Orange 1 free acid, and acid solutions of Oragne 11, F. D. and C Red No. 3 and common wool dyes. The amino group in the cellulose was capable of acid adsorption and of ion-exchange after conversion to a salt.

EXAMPLE 42

The above procedure was followed except that the cellulose films were soaked for only five seconds in the ferrous solution. About 2.1% polymer was deposited. The concentration of the polymer deposition near the surface was shown by dyeing the film with F. D and C Red No. 3, washing, dehydrating, making cross sections and examining the cross sections under the microscope. The red colour was localized near the outer one fifth of the thickness of the cellulose film.

EXAMPLE 43

Poly aminoethylacrylate was deposited into cellulose film using the procedure of Example 24. About 14% of polymer was deposited into the film.

EXAMPLE 44

A 5% solution of agar agar was prepared by dissolving the pure substance in hot water. The solution was poured into a cylindrical mould and allowed to cool to a stiff gel. Discs of about 1 mm. thick were cut from the cylinder and weighed to establish the bone dry weight of the agar agar in the increment of gel.

The discs of gel were steeped for fifteen seconds in 0.1% ferrous solution and washed. The gel discs were then added to 400 ml. of 0.003% hydrogen peroxide containing 20 ml. of methylmethacrylate monomer. The gels which weighed about 0.7-0.9 gm. were then allowed to remain in the monomer solution at room temperature for six hours. When they were washed and dried for several hours under vacuum at 50°C., they were found to have increased in weight by 32%. The gels were of an agar agar which contained about 0.5 milliequivalents of sulphate exchange group per gram of agar agar. When the discs were split with a microtome, it was found that polymer deposition was not present in the interior of the gels. No indication of polymerization in the aqueous phase could be seen. The polymer-modified agar gels were a light greenish yellow colour and were rather brittle.

EXAMPLE 45

The experiment above was repeated except that the saturation of the gel with ferrous iron was done from a solution containing 0.5% ferrous iron as ferrous ammonium sulphate and the pH was adjusted to a pH of about 2 with hydrochloric acid. Similar results to the above were obtained.

EXAMPLE 46

A cellulose sponge whose bone dry weight was about 18 grams was taken and steeped for five minutes in one litre of 0.1% ferrous solution at pH 5. The sponge was washed several times in de-ionized water by squeezing it several times in several batches of clean water. The last wash showed that iron was present.

The ferrous iron impregnated sponge was placed in a two litre container of 0.03% hydrogen peroxide and 20 ml. of *n*-butyl acrylate. Polymerization was allowed to proceed for ten minutes. The supernatant solution remained clear. After drying, the sponge had increased in weight by 20%. The sponge had a light rubbery feel. The dry sponge equilibrated with air was more flexible than a similar dry sponge.

EXAMPLE 47

The above experiment was repeated using *n*-butyl methacrylate. In this instance, the sponge increased in weight by 15.4% and the air-equilibrated sponge did not seem to be quite as "tacky" as the sponge above.

EXAMPLE 48

The above experiment was repeated except that *n*-octyl acrylate monomer was used. A time of polymerization of forty minutes

was also used. The sponge increased in weight by 40%. It was quite tacky to the touch and water had a larger than normal contact angle with the surface. The air-dry sponges were more flexible than control sponges.

EXAMPLE 49

Thin sheets of balsa wood of about one mm. in thickness were taken and steeped for one hour in 0.1% ferrous iron solution. They were washed free of uncombined iron and dropped into a 400 ml., solution of 0.03% hydrogen peroxide containing 10 ml. of methylmethacrylate and allowed to remain at room temperature for twelve hours. In the morning the sheets were washed for several hours and then dried for twelve hours at 80° under vacuum. They were found to have increased in weight by an average of 86%. The sheets were covered with a smooth, seemingly nonporous layer of the polymethyl methacrylate. Cross sections showed that the entire thickness of the wood had been impregnated with the polymer.

EXAMPLE 50

The above experiment was repeated except that the pentachlorophenol ester of acrylic acid was used. Vigorous stirring was also employed to keep the ester suspended. After drying, the wood had increased in weight by 3.4%. It was a slightly yellowish colour, probably due to the oxidized iron. This, as well as the example above, was performed on a known weight of water-extracted wood to avoid the error in the determination of the increase in weight due to water soluble constituents of the wood.

EXAMPLE 51

Polyethylene film about three mils thick was oxidized on its surface by steeping the film for ten seconds in concentrated sulphuric acid saturated with potassium dichromate. Reaction was at room temperature. After washing, the film was found to dye a light blue with the basic dye methylene blue which indicated the presence of at least some carboxyl or other cation binding groups on the surface or within the surface layers.

The oxidized polyethylene was steeped in 0.1% ferrous iron solution at pH 5 for thirty seconds. The excess of solution was wiped off and the treated sheet let stand overnight in 100 ml. of 0.03% hydrogen peroxide and 5 ml. of methyl methacrylate monomer (some of which still floated on the surface of the liquid). When the equal weight increments of film were then dried under a low vacuum and weighed, they were found to have increased in weight by 3.4%. The surfaces were much more hydrophillic than before. In addition, the polyethylene was attached much less readily by such normal solvents as warm mineral oil.

EXAMPLE 52

Polyethylene sheet was oxidized and steeped in ferrous solution as above. This time, the sheet was placed in 200 ml. of boiling 0.03% hydrogen peroxide containing 10 ml. of the methyl methacrylate monomer. Polymerization was continued for fifteen minutes. After washing and drying under vacuum, the films were found to have increased in weight by 4.6%. The surface was wetted to some extent by water as shown by a somewhat lower contact angle and the resistance to attack by nonpolar polyethylene solvents had much increased. Grease penetrated the film much less readily than the control film.

EXAMPLE 53

Polyvinyl acetate was deposited into the surface layers of cellulose film by the procedure of Example 9 except that the film was steeped in the ferrous solution for only five seconds and polymerization was continued for thirty minutes. The films increased in weight by 1.8%. The surface was less hydrophillic than that of the films of Example 9 as shown by the contact angle of a drop of water.

EXAMPLE 54

Cellulose film containing 0.032 milliequivalents of carboxyl per gram of dry cellulose was steeped in 0.1% ferrous solution for one minute and the excess uncombined iron removed by washing.

This film was dropped into 200 ml. of 0.003% hydrogen peroxide solution containing 10 ml. of glacial methacrylic acid. The polymer deposition was allowed to continue for fifteen minutes and the contents of the refluxing solution were dropped into cold water to stop the reaction. No turbidity arose in the aqueous phase when acetone was added to the cooled solution after the polymerization. This, plus salting out tests, showed that no appreciable polymerization took place in the aqueous phase. The equal increments of cellulose film had increased in weight by about 9.2%.

EXAMPLE 55

The above experiment was repeated except that the film was soaked in the ferrous solution for only five seconds. The film increased in weight by only 1.4%. The polymer deposition had been localized to the surface layers of the cellulose film as was shown by dyeing the film with basic dyes and microscopically examining cross sections.

EXAMPLE 56

Wool cloth weighing 0.136 gm./sq. in. which contained no dyes or weighting agents was used for deposition of polymers. The wool was hygrostated at 76% R.H. for several weeks. The moisture content was determined by drying at 60° under vacuum for several hours. In this way, it was possible to take a weight of the wool from the

hygrostat and know the bone dry weight of the wool protein that one actually had.

The wool was steeped in stirred persulphuric acid for thirty minutes. The wool was then washed for thirty minutes with de-ionized water to remove persulphuric acid not chemically combined with the basic groups of the wool. The wool was then added to 400 ml. of water saturated with methyl methacrylate monomer at 80 degrees. The wool was added to the solution and 0.3 gm. of sodium bisulphite also added. Polymer deposition was allowed to continue for twenty minutes. The fabric began to stiffen in about seven minutes. The 0.4—1.5 gm. pieces of modified fabric were washed in water, methanol, and for ten minutes in boiling acetone. After drying for several hours at 115° under vacuum, the fabric pieces were found to have increased in weight by 240% on the average.

Microscopic examination showed that a large amount of polymer was on the surface and that the scales of the wool had been covered completely. Cross sections showed that the central 30% of the volume of the fibre had little polymer deposited into it.

EXAMPLE 57

The procedure of Example 56 was followed except that only a five minute polymerization was used. After drying, the several sets of pieces of fabric had increased in weight by an average of 23%. In this case also, the scales were almost covered and the central 50% of the volume of the wool had relatively little polymer deposited into it.

EXAMPLE 58

Several samples of wool fabric were treated as in Example 56 except that the sodium bisulphite was not added. The wool became yellow and stiff, although not so stiff as those samples of Example 56. The wool had gained in weight by 112%.

EXAMPLE 59

Hygrostated wool fabric was treated with 0.8% persulphuric acid at 50° for ten minutes, washed three times for ten minutes each with demineralized water at 50°C. and heated for thirty minutes at 50°C. with a solution of 1% methyl methacrylate and 0.3 grams of ferrous ammonium sulphate. The wool fibres gained in weight by 9%. There was little polymerization in the aqueous phase. Some polymer was present on the scales of the wool, but it had penetrated only about one fifth of the distance into the wool fibre.

EXAMPLE 60

When the above procedure was repeated without the ferrous iron reducing agent and the polymerization time extended to one hour, the wool lost weight.

EXAMPLE 61

Hygrostated wool was treated at room temperature with 0.8% persulphuric acid for thirty minutes and washed free of excess of reagent not chemically combined, with three ten minute washes with de-ionized water.

The wool was added to a 400 ml. of saturated water solution of methyl methacrylate containing 0.3 grams of ferrous ammonium sulphate. The wool was allowed to remain in the solution for nineteen and one half hours. After removal, washing and drying, the average of the wool samples was a gain in weight of 111%.

Microscopic cross sections showed that the polymer had not penetrated all the way into the wool fibre. The scales of the wool surface were largely covered with polymer.

EXAMPLE 62

Wool fabric was treated as above except that it was steeped in the persulphuric acid for only ten minutes at room temperature. At the end of the reaction time, it had increased in weight by about 14% and cross sections showed that most of the polymer had been restricted in deposition to the outer layers of the wool fibre.

EXAMPLE 63

Wool was treated by the method of Example 61 except that a 5% solution of acrylamide was used as the monomer. The wool increased in weight by 4.5%.

EXAMPLE 64

Wool was treated by the method of Example 61 except that a 5% solution of acrylic acid was used. The wool increased in weight by 13% and the polyacrylic acid was limited to the outer layers of the wool fibre.

EXAMPLE 65

Wool was treated by the method of Example 61 except that a 5% solution of acrylonitrile was used. The wool increased in weight by 6.7%, and was restricted largely to the outer layers of the wool fibre as shown by cross sections.

EXAMPLE 66

Polymethyl methacrylate was deposited into cellulose film by the method of Example 1 for a period of 25 minutes. The film was removed and samples of the equal weight increments dried to determine the amount of polymer deposited. The film was found to have increased in weight by 130%. This film was stiff and showed a Mullen burst strength about 60% above a control film of the same cellulose film from which it had been made.

The moisture vapour permeability of the film was determined with Payne permeability cups and using a constant humidity cabinet with moving, saturated air at 30 degrees. The rate of moisture vapour transfer was found to be one-thirtyfifth of that of a control film of the same thickness under the same conditions.

EXAMPLE 67

A number of equal weight pieces of a pure Manila paper were cut as in Example 3. This

paper had no weighting agent in it. Several small sheets of this paper were dipped in 0.1% ferrous iron solution at pH 5.2 for five seconds. The papers were washed free of uncombined iron and added to a solution of 400 mil. of 0.003% hydrogen peroxide and 10 ml. of methyl methacrylate monomer at the boil. The polymerization was permitted to go for ten minutes and stopped. The dried paper was found to have increased in weight by 11.3%. Examination of cross sections by the staining procedure of Example 8 showed that deposition had been largely localized to the outer layers of the cellulose fibres.

EXAMPLE 68

The procedure of Example 67 was used except that a reaction time of fifteen minutes was used and butyl acrylate was the monomer. The dried films of paper had increased in weight by 8.1%. Diffusion studies of Victoria Blue dye into the fibre indicated localization of deposition near the outer surfaces of the fibre.

EXAMPLE 69

The procedure of Example 68 was followed except that a twenty minute reaction period was used and butyl methacrylate was used as the monomer. The paper increased in weight by 9%. The paper was somewhat tacky as was also that of Example 68. Methylene blue dyeing was less on the outer layers than in the centre of the fibre.

EXAMPLE 70

The procedure of Example 69 was used except that the monomer was acrylonitrile. In this, the paper increased in weight by 7.1%. It did not seem to have changed in appearance. Cross sections of the fibres showed localization of deposition.

EXAMPLE 71

The procedure of Example 67 was followed except that vinyl acetate was used as the monomer and a reaction time of one hour was used. The paper increased in weight by 2.4%, and had become more hydrophobic than normal paper.

EXAMPLE 72

Cellulose film containing 0.04 milliequivalents of exchange capacity per gram of cellulose was steeped for one minute in a freshly prepared 0.1% chromous solution made from chromium potassium sulphate. The pH was 4.1. The film was then washed free of excess chromous ion and immersed in 400 ml. of 0.03% hydrogen peroxide and 10 ml. of methyl methacrylate at the boil under reflux. Polymer was deposited for twenty minutes. The films were found to have increased in weight by 51%, and were a very slight yellow green colour, and were similar in physical properties to the ones prepared with the ferrous iron-hydrogen peroxide reductive activation system.

EXAMPLE 73

The procedure of Example 72 was used except that a 0.1% manganous solution present as manganous sulphate was used. The films increased in weight by 14.7%. They were somewhat less hydrophillic than normal and had a purplish colour.

EXAMPLE 74

0.4 persulphuric acid was prepared by cation exchange using ammonium persulphate. Pure silk fabric weighing 6.67 grams per square foot was procured; the fabric had been hygrostated at 76% R.H. for several weeks. The fabric was dipped in the persulphuric acid for ten minutes and the uncombined acid washed out. The silk fabric was placed in 200 ml. of an 0.3% ferrous ammonium sulphate and 10 ml. of monomer methyl methacrylate. The solution and silk were held at 75° for thirty minutes and washed. The dry silk had increased in weight by 23.5%. Cross sections of the silk dyed and examined under the microscope, showed that polymer deposition had been confined to the outer sixth of the diameter of the silk fibre. Normal acid dyes were used in the cross section staining.

EXAMPLE 75

The above procedure was repeated except that the monomer was vinyl acetate and the reaction time was extended for two hours. In this time, the silk had increased in weight by 18%. Cross sections dyed with acid dyes showed lighter colour near the edges and thus indicated the deposition of blocking polymer in the outer layers of the silk fibre.

EXAMPLE 76

A medium viscosity sodium alginate was made up into a 4% solution in water and films cast into 30% calcium chloride solution containing a small amount of acetic acid. The insoluble calcium alginate films were washed free of excess calcium chloride.

Weights of film corresponding to known weights of calcium alginate were steeped in 0.1% ferrous solution for one minute, and washed. The film was then placed at room temperature in an aqueous solution of 0.003% hydrogen peroxide and 10 ml. of methyl methacrylate monomer. The solution was left at room temperature for twelve hours, removed, and weighed after washing and drying. The gels were found to have increased in weight by 135%.

EXAMPLE 77

The above process was repeated except that the gel films were steeped for only four seconds in the ferrous catalyst solution. Upon washing and drying, the films were found to have increased in weight by 29.4%. Microscopic cross sections treated with the silver deposition method showed the deposition to be localized to the outer portions of the film.

EXAMPLE 78

The process of Example 76 was repeated

except that acrylonitrile was used as monomer. The films increased in weight by 11.4%.

EXAMPLE 79

The procedure of Example 77 was repeated except that acrylonitrile was used as monomer. The film increments increased in weight by 4.3%. The surface was somewhat puckered when the film was dried.

While the conditions required to obtain ion-exchange with ions attached to both weak and strong acids, as well as both weak and strong bases, are well known in the art, the exact conditions required for the most efficient exchange in a particular case would have to be determined by simple routine tests. Generally speaking, a weak acid will make it necessary to work in a weakly acid or nearly a neutral solution of the cation which it is desired to attach to the weak acid group (such as the carboxylic acid group in cellulose). For a dilute solution of the cation and a low exchange capacity of the gel phase, a pH range of about 3.5 to 7.0 is preferred; however, pH levels above 7 can be used providing the cation will remain in solution for an appreciable time at such a pH. As the concentration of cation in the solution becomes high, for example above 5%, the acid concentration which can be permitted, while still obtaining exchange increases.

To obtain exchange of anion in the case of a weak base, like an amino group in cellulose (or the amino or other weak base groups in wool, silk or the like), it is generally necessary to work in an acid solution. Alternatively, if the rate of hydrolysis of the weak base salt is not too high, one could work at low temperatures, soon after the amine salt was formed. Normally, with an amine group of the strength which is found in wool, there is no appreciable anion exchange above a pH of 4.

It has been observed that as the strength of the acid group increases, the amount of acid which is permissible in the solution of the cation, while still getting exchange, also increases. Generally the pH can also be somewhat lower as the concentration of the exchanging cation solution increases. The catalyst cation and the hydronium cation are competing for exchange, so that the extent of exchange will depend both upon strength of the acid group and the amount of the foreign cation which is competing for exchange.

When the ion-exchange group is a strong acid or a strong acid salt, ion-exchange can occur in a relatively strong acid solution even with relatively low concentration of the catalysts cation. Thus, with a divalent catalyst cation, like ferrous iron or manganous ion, one could get some exchange at a pH of 1 or below; using a trivalent catalyst cation like titanous, the amount of acid allowable while still getting exchange would be still greater.

If there is a strong base group in the ion-exchange material, one can get an appreciable anion exchange at a much higher pH than is possible with a weak base anion exchange. Thus with a group like the tetra-alkyl group, one can obtain exchange in a pH of 10 or higher; in such a case, the exchange equilibrium is a competition between the anion in question and the hydroxyl anion. In the case of a divalent anion, like trithiocarbonate, it is possible to get a quantitative exchange with the strong base group even in the presence of as much as 7% sodium hydroxide. A trivalent anion would probably give an even more favourable exchange.

From the above, it is obvious that the conditions necessary to achieve ion-exchange bonding to the cellulose, or other polymer containing such groups of a catalyst cation or anion, can be established with simple tests with the above-described general principles in mind.

With particular reference to the deposition of polymers into cellulose gels in accordance with our novel technique, we find it desirable to use cellulose gels having a low free sulphur content. This is because the presence of relatively small amounts of free sulphur in the cellulose gel can inhibit the polymerization reaction and require an impractically lengthy induction period. If the concentration of free sulphur in the cellulose product which is to be treated in accordance with our invention, is unduly high (for example, if it is about 200 p.p.m.), it may be removed by suitable treatment with sodium or ammonium sulphide, in accordance with techniques well known in the art. In this way, the free sulphur content of a regenerated cellulose film can be reduced to 10 p.p.m. and even lower, in which case the deposition of a polymer such as polymethyl methacrylate into the film shows no discernible induction period. The existence of an induction period would be particularly inadvisable in those situations where polymer is being deposited into the outer layers of a cellulose gel and it is desired to effect a deposition of a high concentration of polymer in a very short time, as in a continuous process.

Different monomers will, of course, have different or perhaps no sensitivity to sulphur, and the amount of sulphur which can be tolerated in the cellulose film will depend upon the monomer used and the time which is allowable for the deposition process.

The temperatures which can be used in practising our invention will be, or course, variable, depending upon the speed of reaction desired, the catalyst concentration in the gel phase, the molecular weight desired in

the polymer deposited into the exchange-group-containing phase, (the molecular weight being generally lower for an increase in temperature), upon the solubility of the monomer, the heat stability of the phase into which the polymer is being deposited, the oxidation ability of the phase into which the polymer is being deposited, and the rate of change of activity of the catalyst system with temperature.

Thus, a material such as wool which is a much denser gel phase than is regenerated cellulose, will require a longer steeping time at a given temperature because the rates of diffusion of ions into cellulose will be much higher than into the dense wool protein phase. The rate of exchange can of course be increased by increasing the diffusion of ions into the gel by increasing the temperature of steeping.

The solvent which is being employed will also have an effect on the time of reaction: thus, at a given ionic concentration, the exchange rate in alcohol, generally, will be lower than when water is used.

If it is desired to limit deposition to an outer layer of the gel, then the diffusion is permitted for only the length of time which will permit ions to diffuse into, and exchange with, the groups in the outer layers of the gel. In the case of a cellulose gel film about 2.5 mils in thickness, exchange with the ferrous solution is usually complete in less than a minute. Generally speaking, in the case of cellulose it is easier to exchange a sodium ion attached to the carboxyl group for the ferrous ion, than it is to exchange it for the hydrogen ion attached to the carboxyl group.

The time of exposure will, of course, also depend upon the thickness of the article to be impregnated or the depth to which one desires polymer deposition to take place. Minimization of polymerization in the solvent phase can be effected by doing the steeping and the polymerization at the same temperature.

The amount of monomer waste which occurs in the process of this invention is markedly less than in prior art attempts at deposition of polymers into a phase from solution or suspension. Most of the time, in the present process, no wastage occurs at all. This is particularly true when the ion-exchange group is a strong acid or base in which the loss of catalyst by hydrolysis is minimized. However, even in the case of weak acid or weak base groups, deposition of polymer in the solution can be minimized and even completely eliminated by working at low temperatures.

Obviously, no hard and fast limits can be placed upon the concentrations of catalyst solutions, ion-exchange group concentration in the gel phase, or the monomer concentration in the solvent or vapour phase outside the phase into which deposition is desired. It is pointed out in this connection that the rate of polymer deposition can be controlled to some extent by controlling the concentration of ion-exchange groups and, therefore, the concentration of the catalyst in the gel phase. Concentration of the cation or anion to be used in the steeping liquor will depend upon the equilibrium constant in the exchange between the catalyst ion and that already attached to the ion-exchange group in the gel phase.

Usually, solutions 0.1%, or less in the catalyst anion or cation will be found effective. Such dilute solutions have several advantages: they show a selectivity for exchange with reference to the ion-exchange group and, in the case of divalent or trivalent cations, they can be kept in solution with lower concentrations of acid; also such solutions permit economy with reference to wastage in washing out the excess.

We wish to point out that in the examples where a particular temperature of steeping is not specified, it is room temperature, namely, between about 23°C. and 26°C.

We also wish to point out that the restriction of deposition by ion-exchange to a given phase, in accordance with our method, is not limited to aqueous systems, since ion-exchange in non-aqueous systems can also occur.

The method of our invention is useful in effecting a substantial improvement in cellulose and other plastic film with respect to such important characteristics as printability, adhesion, heat sealing, decrease in moisture vapour permeability and decrease in static charge. Our process may be used with good results to improve the wet strength, dry flexibility and grease proofness of paper and the like. It will also be seen that fibres of many types can be improved with respect to their dyeing qualities, extensibility, tensile strength, elasticity and resistance to moisture or chemical attack, by treatment of the fibres as per our novel method. Our process is likewise applicable in effecting improvements in certain characteristics of wood so as to effect an increase in its resistance to weathering, rot and the like.

In accordance with the process of our invention, we are able to produce a novel cellulose film which has deposited within the gel phase or localized at the surface layers, polymers of such compounds as ethyl acrylate; p-chlorostyrene; 2,5-dichlorostyrene; N - dimethylamino - ethyl - acrylate; *n* - butyl acrylate; *n*-octyl acrylate; *n*-butyl methacrylate; allyl acrylate; beta-amino-ethyl acrylate and methylene-bis-acrylamide.

Cellulose sponges may likewise be treated in accordance with our invention so as to contain a homogeneous dispersion of a ma-

terial such as poly N,N-dimethylaminoethylacrylate, poly *n*-butyl acrylate, poly *n*-octyl acrylate, poly *n*-butyl methacrylate, and the like.

A weather-resistant and rot-resistant wood can be prepared by depositing thereon in accordance with the technique of our invention a polymer derived from pentachlorophenyl acrylate.

Our invention is also applicable to the production of rot-resistant cotton and rayon. Attempts have been made in the past to improve the rot-resistance of cotton by such techniques as converting cotton cellulose into the cyano ethyl ether having a low degree of substitution; acetylation has also been used. However such procedures while improving the weathering qualities of cotton are expensive, time-consuming, require various kinds of special equipment and are accordingly not entirely satisfactory. In pursuing the solution to this problem, we have made the surprising discovery that we can increase the resistance of cotton to rot by a tremendous factor and without impairing "hand", by depositing a small amount of polyacrylonitrile into the cotton.

Briefly, this technique involves treating cotton so as to form a salt compound with the ion-exchange groupings of the cotton. The cation or anion of the salt compound is selected so that it alone or in combination with an oxidizing or a reducing agent acts as a catalyst for the polymerization of acrylonitrile. The thus-treated cotton is then contacted with a solution or suspension of the monomer alone or with the other member or members of the reductive activation catalyst. The polyacrylonitrile is then deposited by polymerization in the neighbourhood of the catalyst.

This technique is illustrated in the following examples:

EXAMPLE 80

A cotton Osnaberg filter cloth was washed in de-ionized water to which had been added about 0.05% Duponal WA, a wetting agent. It was then rinsed carefully with more de-ionized water, and then air-dried before being put into a hygrostat held at 76% relative humidity. After one week, it was analyzed and found to contain about 5.95% moisture.

Small pieces of the fabric were suitably identified, and then steeped in 0.1% ferrous ammonium sulphate solution at a pH of 5.2 for two minutes. They were then washed in de-ionized water to remove the ferrous iron which had not become chemically combined.

Five of the treated pieces of fabric were then added to a solution of 5% by volume of acrylonitrile in water at 85°C. The solution was immediately made to 0.03% in hydrogen peroxide and was refluxed for 20 minutes; it was observed that the solution did not become even slightly turbid until 15 minutes after the polymer deposition started.

After washing and drying in an oven, the fabrics were found to have increased in weight by an average of 5.41%.

Two pieces of the above-treated filter cloth about 1½" by 5", (which now contained 5.4% polyacrylonitrile) were placed together with two control pieces, untreated, in about 2 kilograms of a slurry made of a mixture of 1 part of soil and 1 part of distilled water. The soil was taken from a vacant lot, and glass and other debris was screened from the soil before use.

The samples of treated and untreated cloth were left in the soil slurry at room temperature for thirty days, the room temperature varying between about 26° and 31°C. The container in which the soil slurry was kept was large enough to have a 500 ml. air space and was sealed to prevent evaporation of water and also to prevent contamination with micro-organisms other than those originally present. After one month, the container was opened and it was found that the untreated cottom was rotted and would almost fall apart in the hands. The strength and appearance of the treated fabric, on the other hand, did not appear to be adversely affected at all.

EXAMPLE 81

The conditions of Example 80 were followed except that 0.1% chromous ion was used for the impregnation of the fabric. The fabric showed a very slight green colour after it was subject to deposition; turbidity in the aqueous phase arose after about 10 minutes of deposition. After the fabric was washed and dried, it was found to have increased in weight by an average of 4.87% and exhibited outstanding rot-resistance compared with a control sample.

EXAMPLE 82

Twenty-four pieces of Osnaberg cotton cloth were cut to a size of about 1½" by 5". The pieces were steeped in 0.1% ferrous sulphate, washed and then dropped in 4 litre flask containing 2 litres of 4% by volume acrylonitrile-water mixture, the mixture being at boiling temperature. The solution was made 0.03% in hydrogen peroxide and deposition of the polymer was allowed to proceed for twenty minutes. Representative samples were dried and found to contain an average of 2% polyacrylonitrile. The samples did not seem to have undergone a change in "hand" and were a very faint yellow in colour.

The remaining pieces were air-dried and on being subjected to the soil burial test previously described were found to have somewhat better resistance to rot than did the control.

EXAMPLE 83

Four small pieces of cotton filter cloth

were steeped for two minutes in 0.1% manganous ion present as manganous sulphate. Excess material which was not chemically combined was washed out and the fabric immediately immersed in a 5% by volume solution of acrylonitrile and water at reflux temperature. Enough ammonium persulphate was added to correspond to the stoichimetric equivalent of the 0.03% hydrogen peroxide concentration previously used, and polymerization was continued for 20 minutes. When the cloths were removed from the solution, washed and dried, they were found to have increased in weight by an average of 8.2% and exhibited excellent rot-resistance.

The protection against rot which the aforesaid treatments offer was completely unexpected because the commercial processes for treatment of cotton for rot-resistance involve cyanoethylation and acetylation of cellulose or treatment of the cotton with potent fungicides or bactericides such as are represented by copper-8-hydroxy-quinolate.

EXAMPLE 84

Cotton cloth was treated by the method of Example 83 except that a 40 minute polymer deposition period was used. The cotton increased in weight by 22%. The particular cotton which was used had an ion-exchange capacity of about 0.013 milliequivalents per gram. Twenty pieces varying in weight from about 0.4 to 1 gram and in various shapes were subjected to the aforesaid procedure. A soil burial test showed complete resistance to rotting for up to two months. The control rotted after twenty days.

The amount of polyacrylonitrile necessary to produce effective resistance against rot is unexplainably much smaller than is required where treatments requiring ether formation are used.

A further advantage of the aforesaid treatment lies in the fact that the technique used results in an introduction of the polymer into the cotton in about 20 minutes, while rot-proofing cotton with other processes which involve say etherification with acrylonitrile, require conventionaly one hour or more of treatment in alkaline solutions to obtain any really significant rot-proofing effect.

A further advantage of our technique is that both catalyst and hydrogen peroxide are used in extremely low concentration and the cost of materials is thus less than the cost of those employed in conventional processes.

While this rot-proofing process works quite well with unbleached cotton, the speed of polymerization could be even further increased by bleaching the cotton under conditions which introduced additional carboxyl groups into the cotton. The process is also applicable for rot-proofing rayon and similar materials.

A raw cotton which has been dewaxed with organic solvents and not kier boiled contains pectin material of polymeric nature so that it shows ion-exchange capacity of 0.03—0.06 milliequivalents per gram of dry cotton. Deposition of polyacrylonitrile by the foregoing processes into such cotton goes much faster than with normal cotton cloth. The speed is over twice that above described.

The present treatment of cotton does not involve an appreciable decrease in strength of the cloth, and gives rise to only a slight difference, if any, in "hand".

Both ferrous and chromous ions can be used as the reducing agents in the present technique and both hydrogen peroxide and ammonium persulphate can be used as the oxidizing members. Furthermore, manganous ion may be used as one component of the redox couple when ammonium persulphate is the other member.

While the deposition of even a small amount of polyacrylonitrile on and in the cotton or rayon has a beneficial effect in imparting rot-resistance, we found that an optimum range of polyacrylonitrile based on the weight of the cloth treated is about 2% to 30% (as measured by the increase in weight of cotton due to polymer deposition). Larger amounts may of course be used, but generally speaking, they result in a harsher texture and a poorer "hand" than when the smaller amounts are used.

The aforesaid rot-proofing technique likewise includes the use of, in lieu of acrylonitrile, such other monomers as acrylic esters, and alkyl acrylates.

The principles of our invention may also be used in the production of articles having other new and useful properties, by the technique of applying a surface layer deposition of a polymer thereby changing the nature of the surface thereof to adhere to other types of coatings such as coatings of the material known under the Registered Trade Mark "Saran". Polymers which can be deposited in this manner, and preferably in high concentrations into the surface layers are illustrated by polyethyl acrylate, polymethyl methacrylate, polyethyl methacrylate, polyacrylates whose alkyl group contains up to 6 carbon atoms and polymethacrylates with the alkyl group containing up to 6 carbon atoms.

The concept involved here, as can be seen, is for the use of hydrophobic polymers for achieving adhesion of hydrophobic coatings thereto.

The useable concentrations of deposited polymers are represented by a very wide range as for example from 2 to 300% or more. Localized deposition into the surface or outer layers of the cellulose gel may be in the range from about 0.1% to 100% or more, based on the total weight of the cellulosic film.

The following examples illustrate this embodiment of the invention.

EXAMPLE 85

Fibrous film composed of cellulose fibres impregnated with regenerated cellulose was steeped for 0.5 seconds in 0.1% chromous ion present as chromous potassium sulphate. It was then placed in a reaction medium consisting of 6 litres of 0.02% hydrogen peroxide containing 100 ml. of pure ethylacrylate, for 15 minutes at the boil and removed therefrom. There resulted a deposition of 4.7% polyethyl acrylate into the film. The resulting treated film was then wetted with a dope having the following composition:

375 ml. of tetrahydro furane
125 ml. of acetone
32 grams of Dow "Saran" F-120, 1000 cps grade powder ("Saran" being a Registered Trade Mark and the material being a copolymer of about 85% vinylidene chloride and 15% acrylonitrile)

The treated film was wetted in this dope for about 20 seconds, drained and the coated films allowed to air dry at room temperature for about 20 minutes. The films were then further dried in the open air under infrared bulbs for 30 minutes at about 80°C. and then at room temperature overnight. Excellent adhesion of the "Saran" F-120 to the modified fibrous film was achieved, and in particular adhesion after a contact with boiling water for three hours was excellent.

The above experiment was repeated using film to which had been applied 10.5% polyethyl acrylate partially localized to the outer portion of the film.

Fibrous film to which was applied from 12% to 38% of polymethyl methacrylate, partially localized to the surface of the film, showed excellent hydrophobicity and excellent adhesion to "Saran" F-120 coating.

The above experiment was repeated using butyl acrylate as the monomer, and 0.1% ferrous solution (as ferrous ammonium sulphate) instead of chromous potassium sulphate. An excellent adhesion of "Saran" to the polybutyl-acrylate coated fibrous film was obtained.

Gels of various kinds can also be prepared containing depositions of various polymeric materials. Thus agar agar gels can be prepared having deposited on the surface thereof or in the gel phase a deposit of a material such as polyacrylonitrile or polymethyl methacrylate. Calcium alginate gels may be prepared having deposited in the gel phase or on the surface such materials as polymethyl methacrylate, polyacrylonitrile, polymethyl acrylate and polyethyl acrylate.

Likewise included in the scope of our invention are other films and film combinations prepared in accordance with the process of our invention; for example, a film of "Pliofilm" (Registered Trade Mark) (rubber hydrochloride) can be readily prepared so that it contains a deposit of polymethyl methacrylate on the surface; likewise a cellulose film containing polyoctyl acrylate in the gel phase or on the surface thereof can also be prepared in the same manner, and be laminated with "Pliofilm" if desired, to produce a composite film structure.

As heretofore mentioned, one of the distinguishing characteristics or features of our invention lies in the fact that it permits limiting the deposition of a polymer to the surface layers or gel phase of the materials being treated. By our method, we are therefore able to produce cellulose film having deposited in the gel phase or on the surface layer thereof, such materials as polystyrene, methyl methacrylate, polyvinyl acetate, polyacrylonitrile, polyacrylic acid, polymethacrylic acid, and polyacrylamide. Polyethylene film having a surface deposition of polymethacrylate can also be prepared in this way.

Animal fibres, particularly wool, can be treated so as to have deposited in the gel phase or at the surface thereof, a deposit of such materials as polyacrylic acid, polymethyl methacrylate and polyacrylonitrile.

Improvements in the characteristics of paper can be secured by treating the paper in accordance with our invention so as to secure thereon a localized deposition of a polymer such as polybutyl acrylate, polybutyl methacrylate, polymethyl methacrylate, polyvinyl acetate and polyacrylonitrile.

Silk may also be advantageously treated in accordance with the method of our invention so as to secure a localized deposition, either in the gel phase or at the surface, of such polymeric materials as polyvinyl acetate and polymethyl methacrylate.

Film materials which are to be used as wrappings or "casings" for food products such as cheese or meat, including sausage, can be prepared by treating the film material, for example, the regenerated cellulose casings of commerce, in accordance with the hereinbefore described methods to modify the moisture-proofness, printability and other characteristics of the base film.

The following examples will serve to illustrate the localized deposition of acrylonitrile into rayon and cotton in accordance with the present invention.

EXAMPLE 86

Rayon continuous yarn, which contained no treating agents and had an ion-exchange capacity of about 0.026 milliequivalents per gram, was pressed flat so that all the filaments were visible and then wound on a rotating drum which was partially immersed in a ferrous ammonium sulphate

solution containing 0.1% ferrous iron at pH 5.2. The drum was rotated at such speed that the yarn was exposed to the catalyst solution for about 0.2 second and was washed immediately after removal from the solution.

The treated fibre was dropped into a solution of 5% acrylonitrile in water at the boil. The solution was made 0.03% in hydrogen peroxide and the mixture refluxed for ten minutes. After the yarn was dried, it was found to have increased in weight by 2%. Its hand did not seem to have been changed appreciably.

The deposition made above was made with a 50:1 solution:yarn ratio.

When the fibre was dyed with an acid dye using the reduced copper technique, it was found that the deposition of the polymer had been limited to the outer third of the "radius" of the fibre.

EXAMPLE 87

The procedure of Example 86 was repeated except that 0.1% chromous ion present as potassium chromium sulphate was used as catalyst. In this case, only a 1.1% increase in weight was noted and the dyed section showing the location of the deposited polymer was limited to the outer one-fourth of the "radius" of the fibre or filament. No polymerization was noted in the aqueous phase in this and the above experiment.

EXAMPLE 88

The procedure of Example 86 is repeated except that manganous ion present as manganous sulphate is used as the cation bound to the cellulose and ammonium persulphate in an amount equivalent to the hydrogen peroxide previously used is the other member of the redox team. In this case, the yarn increased in weight by 3.1% and the polymer is localized to the outer one-third of the "radius" of the film.

The yarn from the three examples above when buried in soil showed greater resistance to rot than the untreated regenerated cellulose yarn from which the modified samples had been made.

EXAMPLE 89

The procedure of Example 86 was repeated except that a polymer deposition period of thirty minutes was used. In this instance, the yarn increased in weight by 9.3%, showed some harshness to the touch, had the polymer deposition limited to the outer third of the filament, and showed outstanding resistance to rotting in moist soil.

The tensile strength, relative to the untreated fibre, was not affected by one month burial, while that of the control sample was greatly reduced.

EXAMPLE 90

The procedure of Example 87 was repeated except that a period of deposition of thirty minutes was used. About 7% increase in weight was noted with the polymer deposition largely restricted to the outer one-fourth of the fibre. The fibres were at least resistant to rot for one month in moist warm soil.

EXAMPLE 91

Rayon yarn was treated by the process of Example 88 but the time was extended to thirty minutes. In this instance, the yarn gained in weight by 13% with the polymer largely restricted to the outer half of the "radius" of the fibres. The fibre had a somewhat harsh hand and was outstandingly resistant to rotting in moist, warm soil.

EXAMPLE 92

An experiment similar to that in Example 86 was performed except that the immersion time of the yarn in the catalyst solution was increased to 0.3 seconds and the deposition time extended to thirty minutes. In this instance, the yarn increased in weight by 24% with the deposition limited to the outer two-thirds of the volume of the fibre and the concentration highest near the surface of the fibre. This fibre, when buried in moist, warm soil, resisted two months' exposure with no loss in strength. It had a harsh feel.

EXAMPLE 93

A cotton yarn when subjected to the conditions of Examples 86, 87 and 88 showed increases in weight of 1.7%, 1%, and 2.3% respectively. The deposition of the polymer was confined to the outer half of the flat thickness of the cotton fibre. The treated cloth endured six weeks soil burial before loss of strength started. A control untreated sample began to lose strength in two to three weeks.

EXAMPLE 94

Procedures analogous to Examples 89, 90 and 91 applied to the cotton yarn above gave rise to deposition of 7.1%, 5.6% and 11% respectively. The polymer was localized to the outer half of the area of the cotton fibre and the resistance to rot compared with untreated cotton was outstanding.

EXAMPLE 95

Cotton yarn was immersed in 0.1% manganous ion present at manganous sulphate for 0.2 seconds using the immersion technique of Example 86. The treated fibres were placed in water containing 5 ml. of vinyl acetate monomer per 100 ml. of solution at the boil. The solution was saturated and had some excess monomer. The solution was made to 0.21% in ammonium persulphate and polymer deposition continued for thirty minutes. The yarn had increased in weight by 12% with the deposition restricted to the outer one-third of the volume of the fibre.

Among the polymer materials which con-

tain ion-exchange groups and which can be treated in accordance with our invention are the following:

Cellulose in pure form and combined with impurities, such as cotton, cotton linters, wood, wood pulp, ramie, hemp, sisal and linen, as well as hemicelluloses, brown algae, bagasse, paper, bacterial cellulose, peat, lignite and tunicin, as well as the various forms of regenerated cellulose.

Others are lichenin, lignin and lignocelluloses, and derivatives thereof which do not destroy the ion-exchange capacity.

Additional materials are represented by cellulose derivatives in which the ion-exchange capacity is not removed. These include inorganic esters like nitrocellulose, cellulose sulphate and phosphate. Organic esters like the acetate, formate, acetate butyrate, acetate propionate, and other fatty acid esters. Unsaturated, halogenated, aromatic and other types of esters may be used. These include cellulose crotonate and methacrylate-acetate, as well as hydroxy, keto and amino esters. Cellulose benzoate and phenylacetyl may also be noted.

Other such materials are condensation polymers which contain an ion-exchange group or which can be made to contain one by hydrolysis or saponification and include nylons, polyesters, phenol-aldehyde, melamine-aldehyde and urea-aldehyde and other condensation polymers containing ion-exchange groups.

Also included are addition type polymers which contain ion-exchange groups including sulphonated polystyrenes, vinyl, acryl, methacryl and allyl ethers, esters, nitriles, amides, acids, acetals, alcohols, alkyl amines, sulphide sulphone, sulphonates, halides, lactams, lactones, carbamates, imides, ketones and mercaptans. Copolymers of monomers containing ion-exchange groups with those which do not may also be considered.

Examples of casing materials which may be used in the process of the invention are:

Regenerated cellulose from the cuprammonium and viscose processes as well as the nitrate, acetate and other processes; alginates, including divalent metal alginates, esters, partial esters, metal salt-ester combinations and other derivatives which do not use up all the carboxyl groups; natural animal casings, including specifically sheep gut casing, beef, hog and other animal casings; regenerated protein casings, including "Naturin" (Registered Trade Mark), "Brechtin", and "Cutecin": low methoxy pectin in which some ion-exchange groups are available; parchment or other paper casing cemented at the edges; casein and chemically-modified insolubilized casein; polyester films in which not all the acid groups have been esterified; amylose casings; addition type polymers or copolymers containing acid or basic groups which have been previously classified.

Other materials containing ion-exchange groups which may be processed in accordance with the principles of our invention are illustrated by the following:

Protein and poteinaceous materials which may be used in the process of our invention include such materials as wool, silk, animal meat casing, skin, leather, gelatin, zein, casein, egg albumin, feathers, peanut protein, regenerated protein, animal hairs, soya and fish protein.

Protein derivatives would include for example acetylated, alkylated, reduced, esterified, cross-linked materials in which some ion-exchange groups were left and formylated, chlorinated salts and isocyanate derivatives.

Starch and starch derivatives would include potato and corn-starch, starch derivatives similar to those of the cellulose and particularly those derivatives which can act as ion-exchange groups in addition to the normal exchange.

Silicone polymers which contain groups capable of ion-exchange are included.

Rubbers, both synthetic and natural, when they contain groups capable of ion-exchange are included. These would include, for example, butadiene copolymers with acid or basic monomers, chloroprene copolymers similarly, partially saponified ester rubbers and urethanes.

Most generally, the ion-exchange anchoring of catalyst may be used with any catalyst which is an anion or cation under the conditions of the impregnation. Organic or inorganic cations or anions may be used.

In addition, redox systems may be used in which one of the essential members of the redox couple is a cation or an anion. In addition, if the third component of the system is a "promoter" and is an anion or a cation, then polymerization may be preferentially secured in the phase in which the promoter is anchored. An example of such anchoring of a promoter would be cupric cation in the redox couple bisulphite-persulphate. Amines which act as "activators" of diene polymerizations would be included in this class if they are present as salts.

Catalysts which may be used if they contain other groups making them cations of anions include, but not exclusively, highly substituted azo compounds, diazo amino, hydroperoxides, aryl substituted paraffins, aryl substituted nitriles, acyl or aryl peroxides, nitroso-acyl-aryl-amines and diazonium salts.

Specific highly active systems described in the literature which may be used include the following redox systems:

An inorganic percompound and some or all of the following reducing cations: ferrous, chromous, manganous, cuprous, titan-

ous and silver ion. The other member of the couple may include such percompounds as hydrogen peroxide, persulphates, perborates and percarbonates.

Other powerful redox systems which may be used include: sulphite-persulphate; sulphate-persulphate; bromate-bromide-sulphites; iodide-cupric and iodide-ferrous with thiosulphate promotion; oxalate-permanganate; hydroquinone-persulphate; benzoyl peroxide-ferrous; cystein-persulphate; chlorate-bisulphite; copper, iron, and silver free metals-persulphate.

Besides the unsaturated monomers hereinbefore listed, it will be clear to those skilled in the art that other monomers may be used, as for example allyl, vinyl, acryl and methacryl monomers containing various functional groups, and including those having primary, secondary or tertiary alkyl groups.

Variations in process steps are of course included in our invention.

Thus, localization of the deposition of a polymer to the outer layers of a formed polymeric structure can also be achieved in the case of a polymer which contains few or no ion-exchange groups. Before the ion-exchange of an article composed of a material such as a nylon, a condensation polymer, an acrylate, methacrylate, or other polymeric esters, the surface of the article may be etched, to effect hydrolysis or saponification, so that ion-exchange groups are released on the surface and in the surface layers. These groups may be used to anchor a catalyst and to deposit a different polymer in the surface layers, as where hardening of the surface is desired.

Ion-exchange with the materials containing such groups can be placed in the same solution containing the monomer, and the catalyst which is thus bound may be subsequently allowed to remain in order to initiate polymer deposition at a low temperature or subsequently or simultaneously the temperature may be raised to start decomposition of the catalyst in the material and deposit the "guest" in the ion-exchange group containing material.

Alternatively, the monomer solution containing one ionic member of the catalyst team and the monomer solution can be used to steep the material containing ion-exchange groups into which the foreign polymer is to be deposited. The other member of the redox team can then later be added.

While the preferred technique of the invention envisions ion-exchange with one member of the catalyst team, immersion in the monomer solution followed by addition to the monomer solution of the other member of the team, the second member of the redox catalyst team may be added before the monomer.

Though our preferred technique of anchoring a catalyst to a polymeric material and subsequently depositing a guest polymer in the polymeric material has special advantages for deposition in the liquid phase, it is not of course limited thereto. Thus exposure to monomer vapour, or monomer vapour plus the second member of the the redox team, of a material in which catalyst placement has been localized to the outer portions of the article can give rise to localized depositions.

Though dilute solutions of monomers are generally used since their use entails less waste in washing, the invention is not limited to the use of dilute solutions only. Concentrated aqueous or organic solutions or dispersions may be used as well as the pure monomer in which the catalyst members need be soluble only if a redox couple is used.

The ion-exchange bonding of the catalyst need not be from the liquid phase. For example the reducing or oxidizing or radical-producing material may be anchored from the gas phase illustrated by the anchoring of ammonia, hydrogen sulphide or sulphuric acid on to strong acid containing materials from the gas phase and the like.

Furthermore, the number of successive treatments of the polymeric material by the process of our invention is not limited. Thus, a film or other article may have deposited into it polymer "A" by the process of this invention, and if the structure is still permeable to a medium which dissolves ions, the original catalyst may be removed and more new catalyst exchanged into the phase and the same or a different polymer "B" added. It is clear of course that the same catalyst system need not be used in both cases.

In addition, one might not use up all the exchange capacity of the polymeric material in the first catalyst impregnation. In such a case, one could then, in the second treatment, use the remaining ion-exchange capacity to bind the same or another catalyst in order to deposit the same or another polymer. A gel or solid polymer containing ion-exchange groups, particularly if it is a hollow article, may have a polymer deposited away from the outside of the object. For example, a cellulosic film tube may be thoroughly impregnated with the catalyst cation or anion and the cation or anion of the surface layers may be removed by washing for a controlled time with an acid or base solution or by inactivation of the catalyst bound to the outer layers by other processes such as oxidation or reduction. The active catalyst remaining in the interior of the gel is then used to deposit a guest polymer in the interior of the gel phase, in this instance near the inside surface of the cellulose tube.

The technique of our invention is applicable to the production of many articles and products other than those heretofore men-

tioned. For example, by the use of our invention, we may produce a fibrous casing having deposited within the paper phase near the interior surface and on the interior surface thereof polymers such as methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl and deca alkyl acrylates and the methacrylates. Such products are characterized by the fact that they have less adhesion to meat which may be encased therein.

The practice of our invention may also be used to produce, for example, a cellulose casing to whose outer layers has been deposited an amino acrylate or methacrylate and which is anchored to a polymer coating by means of a di-isocyanate; the amino compound may include, as an example, beta-amino-ethyl-acrylate and methacrylate. The plastic or rubber polymer coating includes those containing an active hydrogen atom capable of reacting with the isocyanate group. Regenerated cellulose films and fibrous films which have been made hydrophobic with the deposition of a hydrophobic polymer may be coated with polyethylene.

A laminate may be produced by depositing a polymer within a cellulose or cellulosic material and embedding the thus-treated sheet or film in more of the same or similar polymer. Examples of the foregoing are the treatment of wood or plastic sheets with the monomers used in the practice of this invention, and embedding them in the pre-formed plastic material.

Cellulose films may be modified by deposition of a basic polymer throughout or within the surface layers and then dyed with an acid dye to make a fast dyeing. Likewise an acid polymer may be deposited into the cellulose and a basic dye used.

By the practice of this invention polymer films may be treated by depositing therein an appropriate polymer in order to adjust the gas permeability of the polymeric film to a desired value. Likewise we can produce plastic films whose dialysis permeability has been adjusted to a predetermined value by the conrtolled deposition of another polymer within the first.

Film which is suitable for use in the production of laminates of the type described, for example, in Application No. 12029/54 (Specification No. 776,276) may be produced by depositing to the surface of a polymer film another polymer so that the electrostatic charge on the first film is controlled in order to increase the cohesion between the films.

The technique of our invention may also be utilized in producing an electrically non-conducting polymer into which an electrically-conducting polymer has been deposited, by printing on the polymer a deposit of catalyst in the form of a printed circuit.

WHAT WE CLAIM IS:—

1. A method of producing a composite polymeric product, which comprises polymerizing a monomer *in situ* on and/or in a polymeric material which has ion-exchange capacity, in the presence of a polymerization-initiating catalyst system at least partially bonded to the polymeric material by ion-exchange forces.

2. A method as claimed in Claim 1, in which the polymeric material is contacted with a polymerization-initiating catalyst to bond the catalyst to the polymeric material by means of ion-exchange forces and the thus-treated polymeric material is then contacted with the monomer so as to polymerize the monomer *in situ*.

3. A method as claimed in Claim 1, in which the polymeric material is contacted with at least one but less than all of the components of a multiple-component polymerization-initiating catalyst system to bond such component or components to the polymeric material by means of ion-exchange forces and the thus-treated polymeric material is then contacted with the monomer and with the remaining component or components of the catalyst system so as to polymerize the monomer *in situ*.

4. A method as claimed in Claim 3, in which the polymeric material has one component of a free-radical-producing redox couple bound thereto and is contacted with a composition comprising a monomer capable of free-radical-initiated polymerization and the remaining component or components of the redox couple for time sufficient to deposit polymerized monomer in the polymeric material.

5. A method as claimed in Claim 3 or 4, in which the polymeric material is first treated with a fluid containing one component of a free-radical-producing redox couple, uncombined component is removed from the polymeric material and it is then treated with a fluid containing the monomer and the remaining component of the redox couple.

6. A method as claimed in any preceding claim in which a polymeric cellulosic material is employed.

7. A method as claimed in any of Claims 1 to 5, in which the polymeric material is a starch or starch derivative.

8. A method as claimed in any of Claims 1 to 5, in which the polymeric material is a protein or proteinaceous material.

9. A method as claimed in Claim 6, in which the cellulosic material is cotton or rayon, whereby a rot-proofed cotton or rayon product is obtained.

10. A method of rot-proofing cotton or rayon as claimed in Claim 9, in which a polymerization-initiating catalyst is bonded to the cotton or rayon by means of ion-exchange and the cotton or rayon is then contacted with acrylonitrile or a mixture of monomers including acrylonitrile wherein the

acrylonitrile is the major constituent so as to polymerize the acrylonitrile on the fibres thereof.

11. A method of rot-proofing cotton as claimed in Claim 9, in which the cotton is treated with a fluid containing one component of a free-radical producing redox couple, uncombined component is removed from the cotton and the cotton is then contacted with a fluid containing acrylonitrile and the remaining component of the redox couple, whereby the acrylonitrile is polymerized and deposited in the cotton.

12. A method of rot-proofing cotton as claimed in Claim 11, in which chromous ion is the first component of the redox couple.

13. A method of rot-proofing cotton as claimed in Claim 11, in which chromous ion is the first component of the redox couple.

14. A method of rot-proofing cotton as claimed in Claim 11, in which manganous ions is the first component of the redox couple.

15. A method of rot-proofing cotton as claimed in any of the preceding Claims 11 to 14, in which hydrogen peroxide is the other component of the redox couple.

16. A method of rot-proofing cotton as claimed in any of the preceding Claims 11 to 14, in which ammonium persulphate is the other component of the redox couple.

17. A method as claimed in any of the preceding Claims 1 to 6, in which a polymer containing unsaturated groups is deposited in the surface layer of a tyre cord.

18. A method as claimed in any of the preceding Claims 1 to 6, in which the polymeric material is wood fibre, whereby a modified wood fibre product is produced.

19. A method of producing modified wood fibres, which comprises polymerizing an unsaturated monomer *in situ* in wood fibres in the presence of a cationic free-radical-producing, polymerization-initiating catalyst at least partially bonded to acid groups in the wood fibres by ion-exchange.

20. A method of producing a composite polymeric product substantially as hereinbefore described with reference to the foregoing Examples.

21. A composite polymeric product, obtained by depositing a polymer in and/or on a polymeric material having ion-exchange capacity, the concentration of deposited polymer in the product being greatest in the vicinity of the ion-exchange groups of the polymeric material.

22. A composite polymeric product as claimed in Claim 21, which is obtained by polymerizing a monomer in less than the total volume of a solid or gel containing ion-exchange groups.

23. A composite polymeric product as claimed in Claim 21 or 22, in which carboxyl groups comprise the ion-exchange groups of the polymeric material.

24. A composition comprising wood fibres having a polymer deposited therein, the concentration of the polymer being greatest in the vicinity of ion-exchange groups in the wood fibres.

25. A composition as claimed in Claim 24, when produced by a method as claimed in Claim 18 or 19.

26. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising a cellulose film having a polymer deposited within the gel phase.

27. A composite polymeric product as claimed in Claim 26, in which the deposited polymer is a polyacrylate or polymethacrylate.

28. A composite polymeric product as claimed in Claim 27, in which the deposited polymer is obtained by polymerization of N,N-dimethyl-amino-ethyl-acrylate, *n*-butyl-acrylate, *n*-octyl-acrylate, *n*-butyl methacrylate, allyl acrylate or beta-amino-ethyl-acrylate.

29. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising a cellulose film having deposited therein at a predetermined localized situs a polymeric material obtained by polymerization of styrene, *p*-chlorostyrene, 2,5-dichlorostyrene, methyl methacrylate, vinyl acetate, acrylonitrile, acrylic acid, methacrylic acid, acrylamide, octyl acrylate or methylene-bis-acrylamide.

30. A composite polymeric product comprising a cellulose film as claimed in any of the preceding Claims 26 to 29, which is laminated with rubber hydrochloride film.

31. A composite polymeric product as claimed in any of the preceding Claims 26 to 30, in which the deposition is localized at the surface of the cellulose film.

32. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising a cellulose sponge containing a homogeneous dispersion of a polymeric material obtained by polymerization of *n*-butyl-acrylate, *n*-octyl-acrylate or *n*-butyl-methacrylate.

33. A composite polymeric product as claimed in any of the preceding Claims 21, 22, 23 or 26 to 31, comprising a pellicular food casing.

34. A composite polymeric product as claimed in Claim 21 or 22, comprising a film of rubber hydrochloride or of polyethylene having polymethyl methacrylate deposited on the surface thereof.

35. A composite polymeric product as claimed in Claim 21 or 22, comprising a calcium alginate or agar agar gel having deposited within the gel phase a material selected from polymethyl methacrylate, polyacrylonitrile, polymethyl acrylate and polyethyl acrylate.

36. A composite polymeric product as

claimed in Claim 35 in which the polymer is localized at the surface of the gel.

37. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising cotton or rayon having improved rot-proof characteristics produced by depositing therein polymers made from acrylonitrile or acrylonitrile copolymers in which acrylonitrile is the major constituent.

38. A composite polymeric product as claimed in any of the preceding Claims 21, 22, 23 or 37, comprising a rayon or cotton tyre cord.

39. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising wood having deposited therein a polymer derived from pentachlorophenyl acrylate.

40. A composite polymeric product as claimed in Claim 39, in which the polymer is localized at the surface.

41. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising a starch or starch derivative having a polymer deposited thereon and/or therein.

42. A composite polymeric product as claimed in Claim 21, 22 or 23, comprising a protein or proteinaceous material having a polymer deposited thereon and/or therein.

43. A composite polymeric product as claimed in Claim 21 or 22, comprising wool having deposited therein at a predetermined localized situs a polymeric material obtained by polymerization of acrylamide, acrylic acid, methacrylate or acrylonitrile.

44. A composite polymeric product as claimed in Claim 21 or 22, comprising paper having deposited therein at a predetermined localized situs a polymeric material obtained by polymerization of butyl-acrylate, butyl-methacrylate, methyl-methacrylate, vinyl acetate or acrylonitrile.

45. A composite polymeric product as claimed in Claim 21 or 22, comprising silk having deposited therein at a predetermined localized situs a polymeric material obtained by polymerization of vinyl acetate or methyl methacrylate.

46. A composite polymeric product as claimed in Claim 21 or 22, comprising a bast fibre having a polymeric material deposited therein.

47. A composite polymeric product prepared by a method as claimed in any of the preceding Claims 1 to 20.

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Printed for Her Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 684/2.—1959.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

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